CO-PYROLYSIS OF COAL/WASTE POLYMERS MIXTURES

Vlastimil KŘÍŽ * and Zuzana BROŽOVÁ

Institute of Rock Structure and Mechanics, Academy of Science of the Czech Republic, V Holešovičkách 41, 182 09 Prague 8, Czech Republic, tel.: +420 266 009 273, fax: +420 284 680 105
**Corresponding author's e-mail:* kriz@irsm.cas.cz

(*Received* January 2007, *accepted* April 2007)

ABSTRACT
Mixtures of coal/waste tires, coal/waste plastics and coal/waste cotton were pyrolyzed in the laboratory pyrolytical unit built in IRSM AS CR Prague. Non-caking hard coal (mine Lazy) and its mixtures with some organic wastes were pyrolyzed in a quartz reactor inserted in a vertical tube furnace. The main product yields (coke, tar, gas and reaction water) documented exhibit entirely different influence of added waste. Results demonstrated that co-pyrolysis is meaning full in case of waste tiers and plastics. However, in case of co-processing with waste cotton (natural textile), the results are not promising.

KEYWORDS: coal, co-pyrolysis, wastes, cotton, tires, plastics

INTRODUCTION

Organic wastes like scrap tires or plastics represent a significant environmental problem in today's society. The preferred option for its disposal is landfill in most countries. These wastes represent also a potential available source of energy (e.g. their heating value is greater than heating value of most coals). But it is necessary to include exhaust gases purification in case of using technologies based on incineration. Therefore, alternative thermochemical processes seem to be a reasonable and environmentally acceptable method for organic wastes utilization. There have been published some works concerning conversion of organic wastes into fuels or chemical raw materials. The influence of process variables on pyrolysis products (Murillo et al., 2006) has been studied. Yield and composition of products from scrap tires pyrolysis (Williams and Brindle, 2003; Rodriguez et al., 2001) have been reported in the literature. Chemical properties of the pyrolysis liquid product and commercial diesel were compared (Ucar et al., 2005; Walendziewski, 2002). Evaluation of solid, liquid and gaseous products from waste plastics (Walendziewski, 2005) or coal/plastics mixtures (Buchtele et al., 1998) and the possibility of using waste plastics (Tora and Zmuda, 1998) and pitches by coking process (Collin at al., 1997) have been researched in recent years.

In the present work we report on the yield of pyrolysates and chemical composition of coke, tar and pyrolytical gas as a function of loadings of organic additives (wastes) with coal in 15, 30 and 60 %, respectively.

EXPERIMENTAL

Sample collection

Coal sample was collected from Upper Silesian basin, mine Lazy. The proximate and ultimate analyses and their physical properties have been provided in Table 1 and Table 2. The analyses and properties of wastes used are provided in the same Tables. Coal caking properties are documented by the swelling index (SI = 1) and by the dilatometric parameter (b = 18 %) from the Audibert-Arnu test.

Table 1 Characteristics of coal and wastes

	Proximate analysis (wt.%)				Ultimate analysis (wt.% daf)				
	W^a	A^d	VM	S^d_t	C	H	N	S_o	O_d
Hard coal	0.9	6.0	30.8	0.37	83.94	5.00	1.18	0.35	9.53
Waste tires	0.9	5.3	68.9	1.12	85.59	7.65	0.57	1.04	5.15
Waste plastics	0.4	5.4	90.9	0.07	72.76	7.07	0.44	0.06	19.67
Waste cotton	3.8	0.5	92.5	0.09	45.38	6.27	0.52	0.09	47.74

daf: dry, ash free; W^a: water (analytic sample); A^d: ash (dry); S^d_t: sulphur (total, dry)

Table 2 Physical properties of coal and wastes

	Bulk density ($kg.m^{-3}$)	Real density d^d_r ($kg.m^{-3}$)	Gross calorific value Q_s^{daf} ($MJ.kg^{-1}$)	Net calorific value Q_i^{daf} ($MJ.kg^{-1}$)
Hard coal	769	1474	34.50	33.33
Waste tires	323	---	39.92	38.19
Waste plastics	288	1210	33.87	33.32
Waste cotton	37.3	---	18.34	16.98

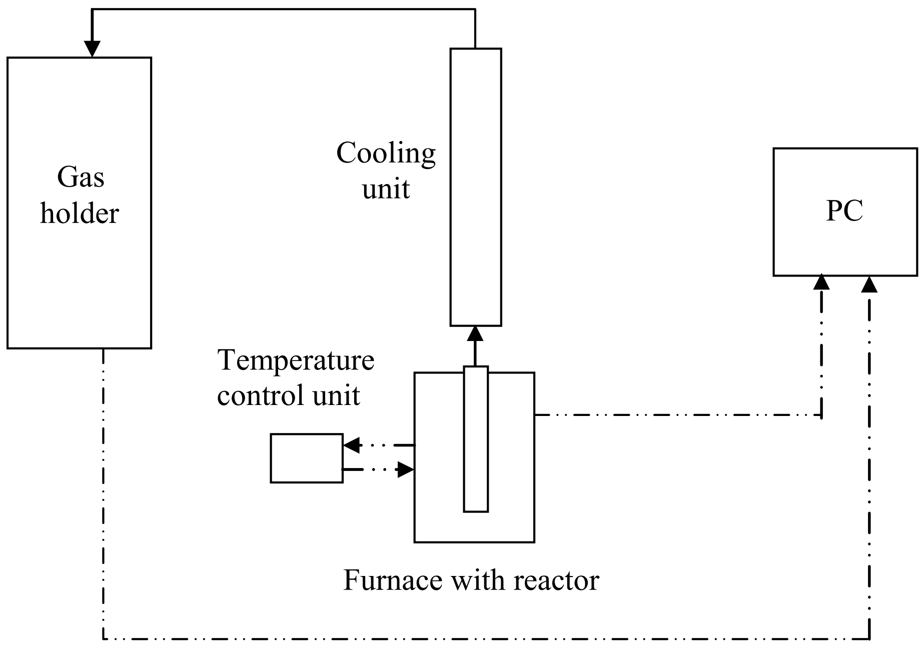

Fig. 1 Functional chart of the laboratory pyrolytic unit

PYROLYSIS

Mixtures of hard coal and selected wastes were pyrolyzed in the laboratory model unit HOR2 (Kříž and Buchtele, 2003) built in IRSM AS CR Prague. Mixed waste plastics, waste tires and waste cotton, as representative organic additives were used.

Pyrolysis of coal alone and its mixtures of 15, 30, 60 % wt. additives were carried out in the quartz reactor inserted in a vertical, temperature micro-processor-controlled, tube furnace under the conditions: Sample weight 150 g; heating rate 5 $K.min^{-1}$ up to 900 °C, soaking time 30 minutes at the final temperature 900 °C. Functional chart of the laboratory pyrolytic unit is shown in Figure 1.

The distribution of matter into solid, liquid and gaseous products of coal alone and coal/waste mixtures pyrolyzed are given in Table 3.

The yields of coke, tar, reaction water and pyrolytical gas are dependent on kind and amount of additive in pyrolyzed mixtures. The yields reflect a good linear dependence on the amount of additive in coal/waste mixtures.

The composition and properties of coke, tar and gas from coal and coal/additive obtained in case of mixtures containing 60 % wt. of additive are given in Tables 4, 5 and 6.

DISCUSSION

One of the aims of the investigation was to carry out the comparison analysis of yields of co-pyrolysis coal/waste tires, coal/waste plastics and coal/waste cotton. Yields of coke, tar, reaction water and gas were evaluated. With regard to different characteristics (Table 1) and physical parameters (Table 2) of used carbonaceous wastes, the yields of products were considerably different. The mixtures: coal/waste tires and coal/waste plastics caused main products coke and tar, which was influenced by relatively lower content of oxygen in additives (tires 5.1 %, plastics 19.7 %) and also in pyrolyzed mixtures. On contrary, waste cotton had a very high ratio of oxygen (47.7 %), and therefore the main products of pyrolysis of its mixtures with coal were coke and reaction water. These differences in the yields are demonstrated in Table 3.

Table 3 Yields of pyrolysis products

	Additive (wt.%)	Yield (wt.%)			
		Coke	Tar	Reaction water	Gas
Hard coal	0	72.6	7.9	4.1	13.2
Waste tires	15	67.9	13.8	3.2	12.3
	30	62.5	20.6	2.7	11.2
	60	52.0	34.2	1.7	9.0
Waste plastics	15	65.2	11.0	6.0	15.0
	30	57.2	16.3	6.5	15.9
	60	41.1	31.6	6.1	17.3
Waste cotton	15	66.8	9.5	8.3	14.0
	30	59.6	10.0	13.8	15.1
	60	44.4	10.9	25.3	17.4

Table 4 Composition and properties of cokes

Additive	Proximate anal. (wt.%)		Ultimate analysis (wt.% daf)					Real density
	A^d	VM	C	H	S_o	N	O_d	($kg.m^{-3}$)
0	8.3	1.3	97.38	0.94	0.45	1.05	0.18	1840
Waste tires	11.1	0.5	97.07	0.64	0.88	0.83	0.58	1871
Waste plastics	14.9	1.5	97.75	0.81	0.45	0.95	0.04	1983
Waste cotton	5.4	1.5	97.30	0.72	0.32	0.88	0.78	1830

A^d: ash (dry)

Table 5 Composition and properties of tars

Additive	A^d (%)	Ultimate analysis (% dry)					Density ($kg.m^{-3}$)
		C	H	N	S	O_d	
0	0.03	83.58	8.27	0.63	0.23	7.26	1040
Waste tires	0.02	81.82	10.48	0.42	0.14	7.12	900
Waste plastics	0.04	81.85	7.94	0.35	0.06	9.76	945
Waste cotton	0.19	56.06	7.12	2.00	0.21	34.42	ND

ND: not determined (heterogeneous sample)

Table 6 Main gas components and properties

Additive	Gas component (vol.%)				Calorific value Qs ($MJ.m^{-3}$)
	H_2	CH_4	CO	CO_2	
0	57.3	22.4	10.0	6.1	20.17
Waste tires	52.3	24.3	9.2	5.6	24.35
Waste plastics	52.0	22.6	8.7	11.2	20.62
Waste cotton	39.4	20.7	21.3	15.8	18.00

INFLUENCE ON COKE AS PRODUCT

Coke is the main product of co-pyrolysis and evaluation of its composition and physical properties gives a real image of its utilization. The increase in amount of coke ash content in coal/tires mixtures (9.3 to 11.1 %) and coal/plastics mixtures (9.6 to 14.9 %) correspond to the content of volatile matter in tires (68.9 %) and waste plastics (90.9 %). Degree of degasification evaluated by H^{daf} content and specific electrical resistance ($\Omega.mm^2.m^{-1}$) in cokes from both mixtures were comparable and suitable. Differences in real density of coke from coal/tires (1848 to 1871 $kg.m^{-3}$) and coal/plastics (1900 to 1983 $kg.m^{-3}$) were caused by relatively higher ash content in cokes from coal/plastics mixtures. Extremely low bulk density of waste cotton (37.3 $kg.m^{-3}$) was the cause of low real density of cokes (1790 to 1830 $kg.m^{-3}$) from coal/cotton mixtures. Their low ash content (A^d round 5.4 %) had only secondary influence on the low real density of cokes obtained in case of coal/cotton mixtures.

INFLUENCE ON TAR AS PRODUCT

The influence of waste tires, mixed waste plastics and waste cotton on tar yield and its properties were studied. It can be seen, that tar yields from co-pyrolysis of tires (34 %), plastics (32 %) and cotton (11 %) are different. They vary in composition and properties as well. Tars obtained from 40/60 mixtures of coal/tires and coal/plastics have practically the same density 900 $kg.m^{-3}$ and 945 $kg.m^{-3}$, respectively. Difference in content of oxygen (7.1 % and 9.8 %) and hydrogen (10.5 % and 8.0 %) shows their different character.

Experiments with usable tars from coal/cotton mixtures were not successful. The reason of it is probably the high oxygen content in waste cotton (O^{daf}_d 48 %), which caused conversion in to the otherwise not useful product i.e. reaction water.

INFLUENCE ON PYROLYTICAL GAS AS PRODUCT

The composition and character of gases from co-pyrolysis of coal/wastes mixtures have quite different progress depending on used additive. It is noteworthy to mention, that it is necessary to evaluate especially components with the greatest share in gas mixture, i.e. hydrogen, methane, carbon monoxide and carbon dioxide. The gas composition from coal/tires mixtures differs least from pyrolytical gas from coal alone. The gas composition from coal/waste plastics mixtures alike in all the parameters studied in case of coal/tires mixtures. The gas composition from coal/cotton mixtures is markedly different from that of coal/tires and coal/plastics. The influence of waste addition is in sequence: tires>plastics>cotton (as well as the composition and character of tars) predetermined by the sequence of oxygen amount O^{daf}_d in mixtures with tires c. 8 % - with plastics c. 13 % - with cotton c. 23 %. It is inferred that additives with oxygen content O^{daf}_d between 40-50 % are quite inapplicable for industrial co-pyrolysis process.

CONCLUSIONS

1. Waste tires and waste plastics could be reused for co-pyrolysis coal/organic wastes.
2. The addition of tires or plastics increases the yield of tar.
3. Waste cotton is not suitable for co-pyrolysis. The reason of which is the high oxygen content in waste cotton, resulting predominantly into reaction water.
4. The solid residue (coke) represents the main product of all experiments. It can be used for production of sorbents or carburizing agents.
5. Hydrogen was the main component of pyrolytical gas obtained in all experiments.

ACKNOWLEDGEMENT

This work was supported by the Institute research plan AVOZ30460519 and by the Czech Science Foundation (GACR) as the project of reg. number 105/07/1407.

REFERENCES

Buchtele, J., Roubíček, V. and Burdová, O.: 1998, Co-processing - Co-pyrolysis of coal with organic wastes, Acta Montana IRSM AS CR, Ser. B, No.8 (110), 29-43.

Collin, G., Bujnowska, B. and Polaczek, J.: 1997, Co-coking of coal with pitches and waste plastics, Fuel Processing Technology, (50), 179-184.

Kříž, V. and Buchtele, J.: 2003, Modelová laboratorní jednotka pro pyrolýzu tuhých paliv a organických odpadů, CHISA 2003, Srní, Sborník 1, 84.

Murillo, R., Aylón, E., Navarro, M.V., Callén, M.S., Aranda, A. and Mastral, A.M.: 2006, The application of thermal processes to valorise waste tyre, Fuel Processing Technology, No.2 (87), 143 – 147.

Tora, B. and Zmuda, W.A.: 1998, The organic waste utilization in the process of synthetic coking coal production, IV Int. Conf. on Clean Technologies for the Mining Industry, Santiago (Chile), Proc. Vol. II, 921-929.

Rodriguez, I.M., Laresgoiti, M.F., Cabrero, M.A., Torres, A., Chomon, M.J. and Caballero, B.M.: 2001, Pyrolysis of scrap tyres, Fuel Processing Technology, No.1 (72), 9-22.

Ucar, S., Karagoz, S., Yanik, J., Saglam, M. and Yuksel, M.: 2005, Copyrolysis of scrap tires with waste lubricant oil, Fuel Processing Technology, No.1, (87), 53-58.

Walendziewski, J.: 2002, Engine fuel derived from waste plastics by thermal treatment, Fuel, No.4 (81), 473-481.

Walendziewski, J.: 2005, Continuous flow cracking of waste plastics, Fuel Processing Technology, (86), 1265-1278.